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### (54) Low voc cleanroom cleaning wipe

Reinraumwischtücher mit niedrigem Gehalt an flüchtigen, organischen Verbindungen

Chiffon pour nettoyage de salle blanche à faible teneur en composés organiques volatils

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**Description****CROSS-REFERENCE TO RELATED APPLICATIONS**

5 [0001] This is a continuation-in-part of US Provisional Patent Application S.N. 60/133,094 filed 7 May 1999.

**BACKGROUND OF THE INVENTION**

10 [0002] The electronics fabrication industry typically requires ultra clean surfaces in fabrication areas, such as clean rooms, due to the extremely small electrical lines and devices and the density of lines and devices that are currently demanded by customers of electronic circuits, such as integrated circuits, typically found in computer chips and memory devices.

15 [0003] Electronic fabrication industry machines and surfaces surrounding the machines and work areas are typically cleaned by wiping down the surfaces with towels, wipes and wipers prewetted with various solvents, wetting agents and cleaning solutions.

[0004] Solutions of isopropyl alcohol (IPA) in water have been used to provide the necessary wetting for efficient cleaning of cleanroom equipment and surfaces such as benchtops. The solutions leave no residue and provide surface tensions of about 45 dynes/cm at ~6 wt% IPA. Although these solutions perform well, the semiconductor industry is under increasing pressure to reduce the emission of volatile organic chemicals (VOC's).

20 [0005] The intense pressure to reduce VOC emissions is of relatively recent origin. US Patent 4,328,279 describes the use of completely non-volatile anionic and nonionic surfactants to enhance the wetting of the fibers in a cleaning wipe. These surfactants would be expected to leave a residue on a cleanroom surface.

[0006] Acetylenic alcohols and glycols have been reported to be effective as additives in cleaning mirrors and lenses in the presence of relatively large amounts of a lower alcohol, such as ethanol and ammonia, see US Patent 4,054,534.

25 [0007] A similar solution was found to be effective for cleaning photoreceptors, as described in US Patent 3,979,317.

[0008] US Patent 3,728,269 describes the use of a mixture of a series of alcohols, including small amounts of 3,5-dimethyl-1-hexyn-3-ol, for cleaning surfaces.

30 [0009] Similarly, US Patent 4,689,168 describes the use of solutions containing 3,5-dimethyl-1-hexyn-3-ol, along with other surfactants in a hard surface cleaning formulation. This disclosure specifically states that the cleaning solution must form an emulsion on agitation.

[0010] US Patent 3,819,522 describes the use of ethoxylated acetylenic glycols in antifogging window cleaners, which require an anionic sulfate to make the glycol acceptable.

[0011] Austrian Patent 257,015 (Chemical Abstract 67:118464) discloses the use of 3,5-dimethyl-1-hexyn-3-ol, along with an amine and non-volatile surfactant for cleaning glass.

35 [0012] Finally, a technical article discusses evaluation of solutions low- and non-volatile organic compounds as replacements for high VOC cleaning formulations in clean rooms; Chemical Abstracts 121:159750, Allison et al., Characterization of Low and Non Volatile Organic Compound Containing Cleaners for Cleanroom Work Surfaces, 1<sup>st</sup> Int. SAMPE Environ. Conf., May 21-23, 1991.

[0013] Acetylenic alcohols are known surface active agents as described in US Patent 4,117,249.

40 [0014] Ethoxylated acetylinic glycols are disclosed in US Patent 5,650,543 as being effective surfactants.

[0015] European patent application EP-A-0 343 304 concerns a wiper comprising a melt blown polypropylene substrate containing a wetting agent, which wetting agent is a functional organosilicone surfactant. In a comparative example thereof the document discloses use of the ethoxylated 2,4,7,9-tetra-methyl-5-decyne-4,7-diols sold under the trademark "Surfynol® 440" and "Surfynol® 465" by Air Products and Chemicals, Inc.. These are considered disadvantageous in comparison to the organosilicone wetting agents taught in said documents. The Surfynols are used in an aqueous solvent in a weight ratio of wetting agent to water of 1 %.

45 [0016] The prior art has attempted to provide an effective clean room wipe, such as represented by US Patent 4,328,279, but has failed to achieve low VOC, low nonvolatile residue (NVR), while avoiding the effects of detergency (foaming), in providing an effective prewetted wipe meeting the criteria of the electronics fabrication industry and the requirements of municipal and national environmental regulations on emissions of various organics. The present invention overcomes the drawbacks of the prior art and achieves the requirements of the electronics fabrication industry and municipal and national environmental regulations in a novel prewetted wipe having unexpected superior performance as will be set forth in greater detail below.

55 [0017] BRIEF SUMMARY OF THE INVENTION

[0018] The present invention is a prewetted cleaning wipe for cleaning surfaces and having low volatile organic chemical and low nonvolatile residue properties comprising a wipe substrate wetted with an aqueous solution of water

and an effective amount of an acetylenic alcohol surface active agent, wherein the ratio of surface active agent to water is in the range of approximately 0.001% to 0.5% by weight.

[0018] Preferably, the surface active agent is an acetylenic diol. More preferably, the surface active agent is an acetylenic glycol. Alternatively, the surface active agent is an ethoxylated acetylenic diol.

5 [0019] Preferably, the surface active agent is dimethyl octynediol. Alternatively, the surface active agent is tetramethyl decynediol.

[0020] Further embodiments are set out in the appending claims.

#### DETAILED DESCRIPTION OF THE INVENTION

10 [0021] Because of regulatory pressures, the electronics fabrication industry are under increasing pressure to reduce emissions of volatile organic chemicals. The present invention has surprisingly found that the use of acetylenic alcohols in aqueous solution allows for efficient surface wetting at greatly reduced levels of VOCs and NVRs.

15 [0022] Historically, solutions of isopropyl alcohol (IPA) in water have been used to provide the necessary wetting for efficient cleaning of cleanroom equipment and bench tops. The solutions leave no residue and provide a surface tension of ~45 dyne km at 6% IPA.

20 [0023] Attempts in the past to conduct such cleaning have dealt largely with the use of traditional surfactants, which can leave a residue or nonvolatile residue (NVR). The acetylenic diols and their various chemical derivatives are volatile and will not lead to a build-up of NVR residues. At the same time, the acetylenic diols and their derivatives are very surface active without foaming properties, allowing them to be used in aqueous solutions at much lower concentrations than previous surfactants, thus resulting in much lower volatile organic chemicals or VOC.

25 [0024] The present invention is directed to the use of completely volatile high surface active wetting agents with ultrapure water prewetted on a wiper. Table 1 shows the efficacy of various acetylenic alcohols and preferably diols, such as Surfynol 61, 82 and 104 available from Air Products and Chemicals, Inc. of Allentown, PA, in reducing the surface tension of water, which provides the necessary wetting for cleaning applications. Much lower quantities of these agents are needed to reduce the surface tension than is the case for isopropyl alcohol. For comparison, the surface tension of 4 wt% IPA is 50 dynes/cm (J. Liq. Chrom. Vol. 10, 1987, pp 561-581).

Table 1

Additive	conc. to give 52 dynes/cm (wt%)
3,5-dimethyl-1-hexyn-3-ol	0.11
dimethyl octynediol	0.20
tetramethyl decynediol	0.004

35 [0025] The acetylenic diols of the present invention include dimethyl octynediol, (Surfynol 82); tetramethyl decynediol (Surfynol 104); ethoxylated tetramethyl octynediol; 2,6,9,13-tetramethyl-2,12-tetradecadien-7-in-6-9-diol; 2,6,9-trimethyl-2-decen-7-in-6-9-diol; 7,10-dimethyl-8-hexadecyne-7,10-diol; 2,4,7,9-tetramethyl-5-decyne-4,7-diol; 4,7-dimethyl-5-decyne-4,7-diol; 3,6-diethyl-4-octyne-3,6-diol; 2,5-dicyclopropyl-3-hexyne-2,5-diol; 2,5-diphenyl-3-hexyne-2,5-diol; 5,8-dimethyl-6-dodecyne-5,8-diol; and various other ethoxylated derivatives where the ethoxylated moiety is 1 to 30 units.

40 [0026] The level of acetylenic alcohol or diol in water is in the range of approximately 0.001% to 0.5% by weight, preferably in the range of approximately 0.01% to 0.3% by wt., and most preferably in the range of approximately 0.05% to 0.2% by wt.

45 [0027] The wipe or towelette substrate which is prewetted with the aqueous acetylenic diol can be a woven or non-woven fibrous sheet. The fibers can be natural fibers, such as cotton or abaca, or the fibers can be synthetic fibers such as polyester, nylon, polyester/cellulose, rayon, polypropylene, rayon/polyester, polypropylene/cellulose, polyurethane, cotton/polyester. The wipe or towelette can be multi-layered or single layered. The wipe or towelette could be in a continuous roll with serated separation seams or they could be individual sheets packaged in a stacked form 50 in a package or sealed container. Each wipe or towelette could be individually packaged in a sleeve or envelope for high purity storage before use. Alternatively, the prewetted substrate could be in the form of a natural or synthetic sponge or pad.

55 [0028] The high purity water is typically a deionized water (DI water) or it can be filtered and distilled for high purity.

[0029] The present invention achieves its unexpected performance in lowering both VOC and NVR by utilizing the ability of these acetylenic alcohols and preferably diols or glycols and their various ethoxylated derivatives to greatly reduce the surface tension of water in comparison to previously used surfactants, while not leaving an involatile residue and while also providing a substantial decrease in the level of VOC's emitted. These acetylenic alcohols and preferably

diols have very high surface active capability and can reduce the surface tension of water to well below 40 dynes/cm and concentrations below 1 wt%. This high surface active property allows the use of correspondingly less surface active agent to achieve the necessary surfactant performance for the cleaning utility. In addition, the acetylenic alcohols and preferably diols have very low foaming characteristics.

- 5 [0030] This approach is superior to that known in the art because it reduces the level of VOCs and NVRs in the cleaning formulation. This is particularly critical to the electronics fabrication industry, such as in the production of semiconductor materials, silicon crystal growing, electronic device fabrication, optical fiber production, integrated circuit production and circuit board fabrication, assembly and packaging.
- 10 [0031] The present invention has been set forth with regard to several preferred embodiments, but the full scope of the present invention should be ascertained by the claims which follow.

### Claims

- 15 1. A prewetted cleaning wipe for cleaning surfaces and having low volatile organic chemical and low nonvolatile residue properties comprising a wipe substrate wetted with an aqueous solution of water and an effective amount of an acetylenic alcohol surface active agent, wherein the ratio of surface active agent to water is in the range of approximately 0.001% to 0.5% by weight.
- 20 2. The cleaning wipe of Claim 1 wherein the surface active agent is an acetylenic diol.
3. The cleaning wipe of Claim 1 wherein the surface active agent is an acetylenic glycol.
4. The cleaning wipe of Claim 1 wherein the surface active agent is an alkoxylated acetylenic diol.
- 25 5. The cleaning wipe of Claim 4 wherein the alkoxylated acetylenic diol is ethoxylated acetylenic diol having an ethoxylated moiety content in the range of 1 to 30 units.
6. The cleaning wipe of Claim 1 wherein the surface active agent is dimethyl octynediol, or tetramethyl decynediol.
- 30 7. The cleaning wipe of Claim 1 wherein the wipe substrate is selected from the group consisting of: cotton, abaca, polyester, nylon, polyester/cellulose, rayon, polypropylene, rayon/polyester, polypropylene/cellulose, polyurethane, cotton/polyester and mixtures thereof.
- 35 8. The cleaning wipe of Claim 1 wherein the surface active agent is selected from the group consisting of: ethoxylated tetramethyl octynediol; 2,6,9,13-tetramethyl-2,12-tetradecadien-7-in-6-9-diol; 2,6,9-trimethyl-2-decen-7-in-6,9-diol; 7,10-dimethyl-8-hexadecyne-7,10-diol; 2,4,7,9-tetramethyl-5-decyne-4,7-diol; 4,7-dimethyl-5-decyne-4,7-diol; 3,6-diethyl-4-octyne-3,6-diol; 2,5-dicyclopropyl-3-hexyne-2,5-diol; 2,5-diphenyl-3-hexyne-2,5-diol; 5,8-dimethyl-6-dodecyne-5,8-diol and mixtures thereof.
- 40 9. The cleaning wipe of Claim 1 wherein the ratio of surface active agent to water is in the range of approximately 0.01% to 0.3% by weight.
- 45 10. The cleaning wipe of Claim 1 wherein the ratio of surface active agent to water is in the range of approximately 0.05% to 0.2% by weight.
11. The cleaning wipe of Claim 1 wherein the wipe substrate is a fibrous substrate, a woven fibrous substrate, a nonwoven fibrous substrate, or a sponge.
- 50 12. The cleaning wipe of Claim 1 wherein the water is high purity water.
13. The cleaning wipe of Claim 1 wherein the water is deionized water.
14. The cleaning wipe of Claim 1 wherein the water is distilled water.
- 55 15. A prewetted cleaning wipe according to claim 1 for cleaning surfaces in an electronic materials fabricating area and having low volatile organic chemical and low nonvolatile residue properties, comprising; a woven fibrous polyester/cellulose wipe substrate wetted with an aqueous solution of high purity water selected from the group con-

sisting of distilled water and deionized water, and an effective amount of an acetylenic diol surface active agent selected from the group consisting of dimethyl octynediol, tetramethyl decynediol and mixtures thereof, wherein the ratio of surface active agent to water is in the range of approximately 0.001% to 0.5% by weight.

- 5      16. The cleaning wipe of Claim 15 wherein the ratio of surface active agent to water is in the range of approximately 0.01% to 0.3% by weight.
- 10     17. The cleaning wipe of Claim 15 wherein the ratio of surface active agent to water is in the range of approximately 0.05% to 0.2% by weight.

#### Patentansprüche

- 15     1. Vorbenetztes Reinigungstuch zum Reinigen von Oberflächen und mit Eigenschaften geringer flüchtiger organischer Chemikalien und nicht-flüchtiger Rückstände, umfassend ein Tuchsubstrat, benetzt mit einer wässrigen Lösung von Wasser und einer wirksamen Menge eines acetylenischen Alkohols als oberflächenaktives Mittel, worin das Verhältnis von oberflächenaktivem Mittel zu Wasser im Bereich von etwa 0,001 % bis 0,5 % in Gewicht liegt.
- 20     2. Reinigungstuch nach Anspruch 1, worin das oberflächenaktive Mittel ein acetylenisches Diol ist.
- 3. Reinigungstuch nach Anspruch 1, worin das oberflächenaktive Mittel ein acetylenisches Glykol ist.
- 4. Reinigungstuch nach Anspruch 1, worin das oberflächenaktive Mittel ein alkoxylierter acetylenisches Diol ist.
- 25     5. Reinigungstuch nach Anspruch 4, worin das alkoxylierte acetylenische Diol ein ethoxyliertes ethylenisches Diol mit einem Gehalt an ethoxylierten Einheiten im Bereich von 1 bis 30 Einheiten ist.
- 6. Reinigungstuch nach Anspruch 1, worin das oberflächenaktive Mittel Dimethyloctindiol oder Tetramethyldecindiol ist.
- 30     7. Reinigungstuch nach Anspruch 1, worin das Tuchsubstrat ausgewählt ist aus der Gruppe, bestehend aus Baumwolle, Manilahanf, Polyester, Nylon, Polyester/Zellulose, Kunstseide, Polypropylen, Kunstseide/Polyester, Polypropylen/Zellulose, Polyurethan, Baumwolle/-Polyester und Mischungen derselben.
- 35     8. Reinigungstuch nach Anspruch 1, worin das oberflächenaktive Mittel ausgewählt ist aus der Gruppe, bestehend aus ethoxyliertem Tetramethyloctindiol, 2,6,9,13-Tetramethyl-2,12-tetradecadien-7-in-6,9-diol, 2,6,9-Trimethyl-2-decen-7-in-6,9-diol, 7,10-Dimethyl-8-hexadecin-7,10-diol, 2,4,7,9-Tetramethyl-5-decin-7,4-diol, 7,4-Dimethyl-5-decin-7,4-diol, 3,6-Diethyl-4-octin-3,6-diol, 2,5-Dicyclopropyl-3-hexin-2,5-diol, 2,5-Diphenyl-3-hexin-2,5-diol, 5,8-Dimethyl-6-dodecin-5,8-diol und Mischungen derselben.
- 40     9. Reinigungstuch nach Anspruch 1, worin das Verhältnis von oberflächenaktivem Mittel zu Wasser im Bereich von etwa 0,01 % bis 0,3 % in Gewicht liegt.
- 45     10. Reinigungstuch nach Anspruch 1, worin das Verhältnis von oberflächenaktivem Mittel zu Wasser im Bereich von etwa 0,05 % bis 0,2 % in Gewicht liegt.
- 11. Reinigungstuch nach Anspruch 1, worin das Tuchsubstrat ein faseriges Substrat, ein gewebtes faseriges Substrat, ein nichtgewebtes faseriges Substrat oder ein Schwamm ist.
- 50     12. Reinigungstuch nach Anspruch 1, worin das Wasser hochreines Wasser ist.
- 13. Reinigungstuch nach Anspruch 1, worin das Wasser entionisiertes Wasser ist.
- 55     14. Reinigungstuch nach Anspruch 1, worin das Wasser destilliertes Wasser ist.
- 15. Vorbenetztes Reinigungstuch nach Anspruch 1 zum Reinigen von Oberflächen in einem Herstellungsbereich für elektronische Materialien und mit Eigenschaften geringer flüchtiger organischer Chemikalien und geringer nicht-

flüchtiger Rückstände, umfassend: ein gewebtes faseriges Polyester/Zellulose-Tuchsubstrat, benetzt mit einer wässrigen Lösung von hochreinem Wasser, ausgewählt aus der Gruppe, bestehend aus destilliertem Wasser und entionisiertem Wasser, und einer wirksamen Menge eines acetylenischen Diols als oberflächenaktives Mittel, ausgewählt aus der Gruppe, bestehend aus Dimethyloctindiol, Tetramethyldecindiol und Mischungen davon, worin das Verhältnis von oberflächenaktivem Mittel zu Wasser im Bereich von etwa 0,001 % bis 0,5 % in Gewicht liegt.

- 5      16. Reinigungstuch nach Anspruch 15, worin das Verhältnis von oberflächenaktivem Mittel zu Wasser im Bereich von etwa 0,01 % bis 0,3 % in Gewicht liegt.
- 10     17. Reinigungstuch nach Anspruch 15, worin das Verhältnis von oberflächenaktivem Mittel zu Wasser im Bereich von etwa 0,05 % bis 0,2 % in Gewicht liegt.

#### Revendications

- 15     1. Moyen d'essuyage nettoyant prémouillé pour nettoyer des surfaces et ayant des propriétés de faibles teneurs en produits chimiques organiques volatils et de faibles teneurs en résidus non volatils comprenant un substrat de moyen d'essuyage mouillé avec une solution aqueuse d'eau et d'une quantité efficace d'un agent tensioactif alcool acétylénique, où le rapport de l'agent tensioactif à l'eau est dans la plage d'approximativement 0,001 % à 0,5 % en masse.
- 20     2. Moyen d'essuyage nettoyant selon la revendication 1 où l'agent tensioactif est un diol acétylénique.
- 25     3. Moyen d'essuyage nettoyant selon la revendication 1 où l'agent tensioactif est un glycol acétylénique.
- 30     4. Moyen d'essuyage nettoyant selon la revendication 1 où l'agent tensioactif est un diol acétylénique alcoxylé.
- 35     5. Moyen d'essuyage nettoyant selon la revendication 4 où le diol acétylénique alcoxylé est un diol acétylénique éthoxylé ayant une teneur en groupements éthoxylés dans la plage de 1 à 30 unités.
- 40     6. Moyen d'essuyage nettoyant selon la revendication 1 où l'agent tensioactif est le diméthyloctynediol ou le tétraméthyldécynediol.
- 45     7. Moyen d'essuyage nettoyant selon la revendication 1 où le substrat de moyen d'essuyage est choisi dans le groupe consistant en : coton, abaca, polyester, nylon, polyester/cellulose, rayonne, polypropylène, rayonne/polyester, polypyropylène/cellulose, polyuréthane, coton/polyester et leurs mélanges.
- 50     8. Moyen d'essuyage nettoyant selon la revendication 1 où l'agent tensioactif est choisi dans le groupe consistant en : tétraméthyoctynediol éthoxylé ; 2,6,9,13-tétraméthyl-2,12-tétradécadién-7-yne-6,9-diol ; 2,6,9-triméthyl-2-décén-7-yne-6,9-diol ; 7,10-diméthyl-8-hexadécyne-7,10-diol ; 2,4,7,9-tétraméthyl-5-décyne-4,7-diol ; 4,7-diméthyl-5-décyne-4,7-diol ; 3,6-diéthyl-4-actyne-3,6-diol ; 2,5-dicyclopropyl-3-hexyne-2,5-diol ; 2,5-diphényl-3-hexyne-2,5-diol ; 5,8-diméthyl-6-dodécyne-5,8-diol et leurs mélanges.
- 55     9. Moyen d'essuyage nettoyant selon la revendication 1 où le rapport de l'agent tensioactif à l'eau est dans la plage d'approximativement 0,01 % à 0,3 % en masse.
- 60     10. Moyen d'essuyage nettoyant selon la revendication 1 où le rapport de l'agent tensioactif à l'eau est dans la plage d'approximativement 0,05 % à 0,2 % en masse,
- 65     11. Moyen d'essuyage nettoyant selon la revendication 1 où le substrat de moyen d'essuyage est un substrat fibreux, un substrat fibreux tissé, un substrat fibreux non tissé ou une éponge.
- 70     12. Moyen d'essuyage nettoyant selon la revendication 1 où l'eau est de l'eau de haute pureté.
- 75     13. Moyen d'essuyage nettoyant selon la revendication 1 où l'eau est de l'eau désionisée.
- 80     14. Moyen d'essuyage nettoyant selon la revendication 1 où l'eau est de l'eau distillée.

15. Moyen d'essuyage nettoyant prémouillé selon la revendication 1 pour nettoyer des surfaces dans une zone de fabrication de matériels électroniques et ayant des propriétés de faibles teneurs en produits chimiques organiques volatils et de faibles teneurs en résidus non volatils, comprenant : un substrat de moyen d'essuyage en polyester/ cellulose fibreux tissé mouillé avec une solution aqueuse d'eau de haute pureté choisie dans le groupe consistant en l'eau distillée et l'eau désionisée, et d'une quantité efficace d'un agent tensioactif diol acétylélique choisi dans le groupe consistant en le diméthylctynediol, le tétraméthyldécyanediol et leurs mélanges, où le rapport de l'agent tensioactif à l'eau est dans la plage d'approximativement 0,001 % à 0,5 % en masse.
16. Moyen d'essuyage nettoyant selon la revendication 15 où le rapport de l'agent tensioactif à l'eau est dans la plage d'approximativement 0,01 % à 0,3 % en masse.
17. Moyen d'essuyage nettoyant selon la revendication 15 où le rapport de l'agent tensioactif à l'eau est dans la plage d'approximativement 0,05 % à 0,2 % en masse.

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